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RADIATION DAMAGE TEST ON EPOXIES FOR COIL INSULATION

E. Laukant

July 1969



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1. INTRODUCTION

This test program was initiated to find radiation resistant epoxy systems to be used as insulating materials for magnet coils at NAL.

While previous studies report on radiation resistant epoxies, this study includes in addition to the radiation resistance data to find the best compromise to obtain practical application by:

- (a) Vacuum impregnation
- (b) B-stage epoxy-fiberglass tapes
- (c) Room cured epoxies

Electron beam irradiation was chosen since a high dose level can be reached in a short time. The irradiation was performed with the 1.5 MeV Dynamitron at Radiation Dynamics, Inc. on Long Island, New York.

Two consecutive irradiation tests were conducted. The first test served as comparison of the electron beam to the published reports on radiation damage, performed with other particle beams. Also new resin-hardener combinations were chosen which had not been tested.

The second test served to provide more detailed and accurate data to complement the first test. Resins and

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hardeners tested in this program are listed on Tables 1 and 2.

2. SPECIMEN AND IRRADIATION CONDITIONS

To cool the sample during irradiation, maximum heat conduction from the specimen had to be achieved. For this purpose a .04" thick glass tape reinforced epoxy sheet was cured to a 0.0015" thick copper sheet. The specimens with their copper backing were cut to size and then soldered to a water cooled heat sink. A 204°F melting point solder was used in order not to thermally degrade the epoxy.

During the irradiation process a dose rate of 1.5 megarads per second was maintained and the specimen temperature reached about 75°C. The temperature was measured with two thermocouples.

For the first test vacuum impregnated specimens of the size 0.04" x 0.5" x 1.0" were prepared. The glass reinforcement consisted of five layers of 0.007" thick plain medium weave Volan treated glass tape. Five specimens each were irradiated at six integrated dose levels of up to 2 x 10^{11} rads. The epoxy systems were numbered 1 to 18.

Specimens for the second irradiation run were made of the size 0.04" x 0.25" x 1.25". They were vacuum impregnated and used seven layers of 0.007" thick amino silane treated glass tape. The epoxy portion of this laminate was less than 30 percent by weight. The highest integrated irradiation dose was increased this time to 5×10^{11} rads. The epoxy systems were numbered 21 to 44.

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3. DEFLECTION TESTS

The first irradiated specimens were tested as simply supported beams by measuring <u>FIBER STRESS</u> at a deflection of 0.02" using a span of 0.5". This furnished only comparative test results, which are not per ASTM Standards because of the specimen size. However, the test results revealed that most of the epoxy systems cured with aromatic amines broke, as noted on the tables and figures, while no sample broke which had been cured with methyl Nadic anhydride (MNA). The former specimens had blisters after irradiation but none of the latter were blistered.

Flexural strength tests were then made on the better epoxy systems, see Figures 1 to 18.

Specimens which were irradiated at the second test had a physical size that conformed to ASTM Standards for flexural strength, see Figures 21 to 44.

The tangent modulus was calculated from the flexural strength graph to indicate the stress/strain relationship.

4. WATER ABSORPTION AND WEIGHT LOSS

Irradiation causes the epoxy to become brittle and finally disintegrate into a black powdery substance. It increases the amount of water which the system can absorb.

The irradiated specimens of the second test run were cut to 0.5" lengths and immersed in boiling, distilled water for 24 hours. The weight was determined immediately after

drying with paper cloth. The percentage water absorption was calculated after subtracting the weight of the glass cloth, since the water absorption is assumed to occur only in the epoxy. This water absorption test conforms to ASTM D570-63.

The percent weight loss was also calculated on the basis of the epoxy portion only. The graphical representation is shown in Figures 21 to 44, and comparatively presented in Figure 45.

Water absorption was from 15% to 35%, and weight loss was from 0% to 32% at 10^{11} rads irradiated dose level.

5. IMPACT TEST

Epoxies which prove to be radiation resistant are generally brittle and would crack easily when used for coil insulation.

In an attempt to achieve tougher systems, resins were combined with stoichiometric, deficient and excessive ratios of curing agent.

The impact strength was measured with the Mineola pendulum cantiliver beam impact testing machine of Izod type. The test was made on cast half inch wide epoxy bars as per ASTM D256-56.

The impact tests revealed some deviations which cannot be explained as a rule. Epoxy 29 indicated the largest deviation. The values are from 0.122 to 0.436 ft-lb/inch, Table 5. An impact strength of 0.50 ft-lb/inch is desired for coil insulation.

Although the resin/hardener ratio has some effect on the plasticity there seems to be no deviation in radiation resistance, Figures 21, 22, 23.

6. OVERLAP SHEAR TEST

The objective of this investigation was to find the bond strength of epoxy to copper.

Two copper strips $0.062" \times 1" \times 6"$ were wetted on one end with epoxy. The strips were then assembled in a fixture with 0.5" overlap and cured. The lap shear strength was determined by pulling the samples apart in a tensil testing machine. The values ranged from 437 psi to 1329 psi, see Tables 3 and 4.

7. VISCOSITY

For vacuum impregnation the lowest possible viscosity is desired. All the specimens were prepared by vacuum impregnation, and therefore the viscosity of all systems is satisfactory. Comparison tests with standardized liquids were made of the epoxies at room temperature and at 66°C, see Table 4.

8. POT LIFE

Epoxies with a 10 hour pot life at vacuum impregnation temperature, (usually 45°C), are desired for large coils. The longest pot life stated is 24 hours since it was observed only for that time. Data on pot life at room temperature are given in Table 3. The pot life at room temperature and at 66°C is given in Table 4.

9. CURING CYCLE

In order to determine the proper curing cycle, maximum glass transition temperature (GTT) of the epoxy was found by consecutive post-curings. For the first irradiation test the epoxy systems were cured to the ultimate GTT. How-ever, the curing cycle may be considered adequate when the cured epoxy cannot be attacked by acetone. Therefore the second irradiation test, the epoxies were cured for a minimum curing cycle determined by this criteria.

10. GLASS TRANSITION TEMPERATURE (GTT)

Previous study^{2 - 3} have shown that epoxy systems with higher GTT, or Heat Distortion Temperature, frequently have high temperature stability and are more radiation resistant.

On Table 4 the GTT is shown in two columns: the tested value of the epoxy at specified curing cycle and the ultimate GTT. See the ultimate GTT also on Table 3 and Figure 45 for comparison.

11. CONCLUSION

Resins: Diglicydyl ether of bisphenol A resins

(DGEBA) resist radiation well. However, if the GTT is taken
as a criteria, they are not the best. The tested DGEBA resins
rank in the following order of decreasing radiation resistance:

DER332LC, DER332, EPON 826, EPON 828; i.e. purer resins show
better radiation resistance.

The Cycloaliphatic resins used have very low viscosity.

They could be utilized advantageously for vacuum impregnated,

and filler loaded coil insulation systems. Following a previous study¹ the investigation of ERL 4206 was continued in this test program. When the resin is cured with 841 the epoxy is exceedingly brittle, perhaps due to incomplete cure. The specimen blistered during irradiation. MNA as hardener is the best choice. The viscosity of this epoxy is below 90 centipoises, and the radiation resistance is good. The highest GTT of this epoxy system with a deficient quantity of MNA (115 phr) is 252°C. Decrease of hardener increases the brittleness and the resistance to radiation.

The Glycidyl Amines, tetraglycidyl 4.4' diaminophenylmethane (x8183/137) and trigylcidyl para-amino-phenol
(ER 0510), both are top quality resins for radiation resistant
epoxy systems. Their GTT and temperature stability is high,
but the epoxy is also brittle.

The Novalac resin ranks among the best⁴ of all the resins. The high viscosity, however, does not permit many useful application techniques. The Novalac performs well when combined with the aromatic amine as hardener. Even a fairly high degree of plasticity can be reached with this combination. The Novalac resin is also used for B-stage epoxy, samples 29-36.

<u>Curing Agents</u>: Previous studies¹⁻⁴ show that the radiation resistance of epoxy systems when cured with aromatic amine hardeners are superior to the non-aromatic analogues.

This study shows, however, that epoxy systems with

aromatic amines, when tested by flexural strength, reveal a loss of strength at moderate irradiation dose levels and an increase at high dose levels. If such an epoxy system would be used for coil insulation, it might break down at lower dose levels on account of its low physical strength.

The second disadvantage is that the most tested of the aromatic amine cured systems blister due to gas evolution² during the irradiation process. This is in accord with previous work.³ If such an epoxy is used for coil insulation the coil might deform.

However, an exception to the rule is the eutectic amine compound EPI-CURE 841 hardener when combined with the Novalac resin, see Figure 29.

The aromatic amines used increased the viscosity and generally gave a short pot life.

This study shows that glycidyl amine, cycloaliphatic and DGEBA resins are best when combined with an anhydride as curing agent whereas the Novalac resin is best when combined with an aromatic amine.

All aromatic amines when heated to decomposition will produce highly toxic fumes. OTOL, DMB, and DAN are suspected carcinogens. 6

In general best of all the hardeners tested is MNA.

All the figures show a gradual decrease in flexural strength.

MNA reduces the viscosity, gives a long pot life and is not toxic.

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Epoxy Accelerator: BDMA has a vapor pressure of 120mm Hg at 130°C. Therefore it could not be used for vacuum impregnation because it might boil off.

DB VIII has a vapor pressure of 10 mm Hg at 175°C, and therefore is recommended for vacuum impregnation.

While one percent of BDMA added to the total amount of the epoxy system is adequate; two percent of DB VIII are needed.

12. SUMMARY

Resins with decreasing radiation resistance respectively are:

Novalac

Glycidyl Amine

Cycloaliphatic

DGEBA

Usable curing agents are:

MNA

EPI CURE 841

EM 308 for room cured epoxy

Room cured epoxy can show excellent resistance to radiation. Room cured tests seem to prove once more the good qualities of the glycidyl amine resin, Figures 37, 38.

Cracking of brittle, radiation resistant epoxies can be reduced by adding inorganic filler materials. The filler can be glass tape, glass beads, alumina powder or mica.

This report provides the coil manufacturer with several choices of epoxy systems applicable for vacuum impregnation,

B-stage application and room cured epoxies. The final choice of the epoxy will be a compromise between viscosity, pot life, curing cycle, plasticity and bond to copper.

Since no gas blisters could be detected on the Novalac/ aromatic amine epoxy system it is retained for further investigation especially with the long pot life hardener diaminodiphenylsylfone.

13. ACKNOWLEDGEMENTS

The author wishes to express appreciation to Finley
Markley of the Argonne National Laboratory. Many hours of his
friendly consultation contributed greatly to this study
program. All the work was done in his laboratory. Acknowledgements are due to the companies who sent test samples, resins
and hardness, and to Robert Jensen for preparing and performing the tests.

14. REFERENCES

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- 3. I.D. Aitken and K. Ralph, Some Effects of Radiation in Cast Epoxide Systems, AERE-R 3085 (1960).
- 4. G. Pluym and M. Van de Voorde, Radiation Damage Tests on Epoxy Resins (1967).
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TABLE 1

DESIGNATION, MANUFACTURER AND EPOXIDE EQUIVALENT OF RESINS

Designation	Manufacturer	Epoxy Equivalent (approx)
X 8183/137 in USA is X 33/1020, is Glycidyl Amine in Europe	CIBA	127
ERL 0510	Union Carbide	99
ERL 4206	Union Carbide	76
DER 332 LC	Dow	173
DER 332	Dow	174
DEN 431 Novalac	Dow	175
DEN 438 Novalac	Dow	179
EPON 826	Shell	184
EPON 828	Shell	188
R9-2039	Hysol	190
x 50	Bayer	120
У 663	Sterling (Epoxy system)	
N.E.C1	National Electric Coil Co. (Epoxy system: DGEBA + BF ₃ + glass tape with mica paper as filler)	
N.E.C2	National Electric Coil Co. (Epoxy system: DGEBA + BF ₃ + glass tape with 3000 mesh mica powder)	
3M-1, 3M-2, 3M-3, 3M-4, 3M-5	Minnesota Mining & Mfg. Co. (Novalac Epoxy systems)	

Chemical Name	Abbreviation	Supplier
	'	
Eutectic amine compound	EPI CURE 841	Celanese
Diamino-diphenyl-methane	DDM	Dow
Diamino-diphenyl-sulphone	DDS	Merck
O-tolidine (3,3' dimethylbenzidine)	OTOL	Eastman
3,3' dimethoxy-benzidine	DMB	Aldrich
1,8 diamino-naphtalene	DAN	Aldrich
Meta-xylylene-diamine	MXDA	Aldrich
Reactive Modifier	ЕМ 308	Thiokol
Methyl-Nadic-anhydride	MNA	Union Carbide
Boron-trifluoride	BF3-MEA	Aldrich
Modified amine	н2-3561	Hysol
Amine adduct	н8-3485	Hysol
Benzyl-amine	BA	Matheson
Benzyl-dimethylamine	BDMA	Maumee
None-aromatic accelerator	DB VIII	Argus
Phenol		Fisher

T, .E 3

COMPOSITION, CURING CYCLES AND TEST DATA FOR EPOXY SYSTEMS

Broke at test	ou	ou	ou	ou	ou	yes	ou	yes	yes	yes	yes	yes	yes	yes	ou	yes	yes	Yes
Blisters	yes	ou	no	ou	yes	Yes	ou	yes	yes	yes	yes	yes	yes	yes	ou	yes	ou	ou
Shear Strength PSI	687	502	402	388	477	859	1280	982	1066	1329	701	1032	066	1292	574	437		
Ult. GTT (°C)	246	225	202	255	244	238	128	180	133	204	150	172	174	157	247	203		
Curing Cycle hours - °C	10-100	24-160	4-80, 36-150	1-100, 5-160	1-100, 5-160	1-100, 5-160	4-80, 15-150	4-165	1-130, 4-150	6-150	1-100, 2-200	4-165	6-150	6-150	5-100, 36-160	10-100, 30-150		
Pot Life (hours)	4	24	24	ιΩ	Ŋ	24	24	10	24	24	10	10	ស	υ	10	24		
Accele- rator (phr)	Ī	ı	ı	I	l	ı	DB VIII (5)	l	i	ı	i	ı	ı	1	DB VIII (5)	1		
Curing Agent (phr)	DDM (40)	DAN (32)	MNA (150)	841 (43)	OTOL (56)	DAN (40)	MNA (90)	DDM (28)	BF ₃ (3)	DDS (34)	841 (25)	DDM (28)	OTOL (30)	DMB (34)	MNA (205)	841		
Resin	X 8183/137	X 8183/137	ERL 0510	ERL 0510	ERL 0510	ERL 0510	DER 332	DER 332	DER 332	DER 332	EPON 826	EPON 826	EPON 826	EPON 826	ERL 4206	ERL 4206	N.E.C1	N.E.C2
Sample Number	Н	7	ო	4	Ŋ	9	7	œ	6	10	11	12	13	14	15	16	17	18

TABLE 4

COMPOSITION, CURING CYCLES AND FEST DATA FOR EPOXY SYSTEMS

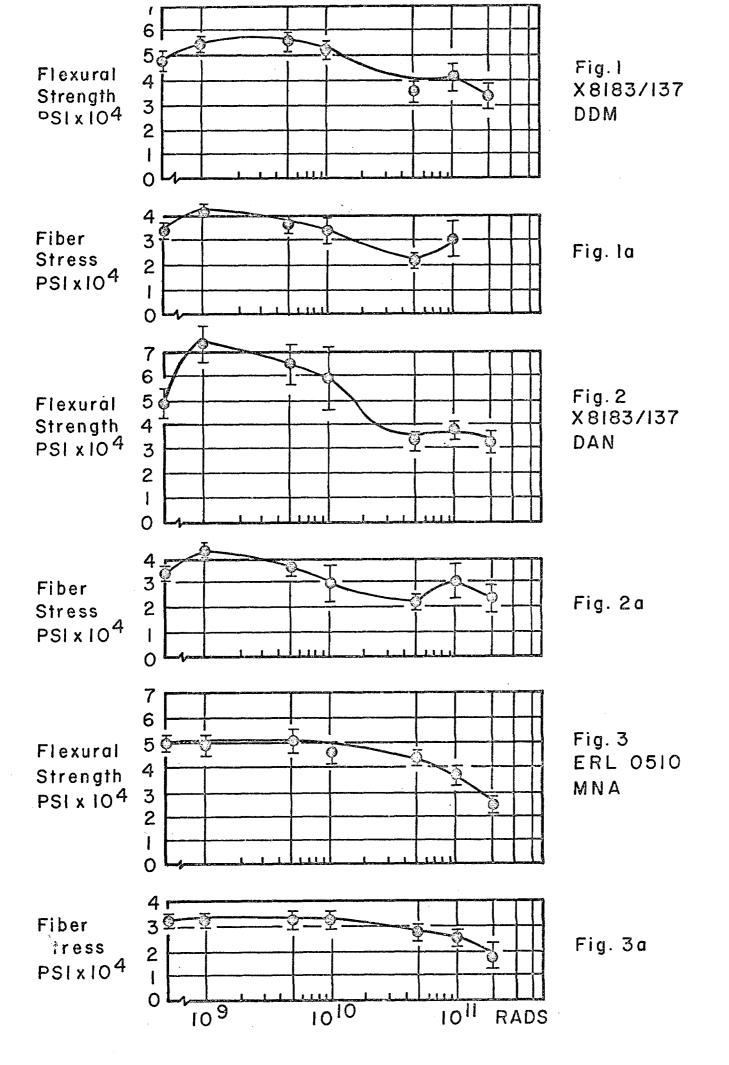
	_		-	-	-	Pot-Li	fe Fe			,			ù
GE TC		\$ \$ \$ \$	()	Viscos	sity	(hours)	(8)		(-	; ; ;	, se .	: 6 7:
qmau dmuN	Resin	Curing Agent (phr)		room temp	at 66°C	EΩ	at 66°C	Curing Cycle hours - °C	Cure GTT	GTT °C	snear Strgth PSI	Impact Strength ft-1b/inch	siI8
21	DER 332 LC	MNA (90)	BDMA (1.9)	008	400	24	4	4-80, 10-125	147	163	743	.284 ± .031	no
22	DER 332 LC	MNA (60)	BDMA (1.6)	800	400	24	4	4-80, 10-125	107	132	1033	.288 ± .047	no
23	DER 332 LC	MNA (130)	BDMA (2.5)	800	400	24	4	4-80, 10-125	127	151	963	.254 ± .042	ou
24	DER 332	MNA (90)	BDMA (1.9)	800	400	24	4,	4-80, 10-125	133	146	830	.310 ± .104	no
25	EPON 826	MA (90)	BDMA (1.9)	800	400	24	4	4-80, 10-125	118	143	830	$.294 \pm .070$	ou
26	EPON 826	841 (12) + BA (11)	l	800	400	24	1.5	2-100, 24-150	109	119	969	.438 ± .126	no
27	R9-2039	H8-3485	ı	400	200	24	24	12-100	61	75	1206	1	yes
28	X663	ı	1	1	ı	l	ŀ	2-175	1	ı	I	ı	yes
29	DEN 431	841 (17)	I	1200	200	20	3.5	2-100, 22-160	170	180	564	.436 ± .132	no
30	DEN 431 m	MNA (57)	BDMA (1.7)	1200	200	24	24	2-100, 22-160	133	249	830	.289 ± .058	no
31	DEN 438 .1	MNA (85)	BDMA (1.9)	1200	200	20	10	2-100, 22-160	152	268	762	.246 ± .028	no
32	3M-1	l	ı	1	1	1	ı	3-120, 5-175	153	226	820	1	no
33	3M-2 0	ı	1	ı	1	ı	ı	3-120, 5-175	136	235	099	ľ	no
34	3M-3	ı	1	ı	l	i	1	3-120, 5-175	215	230	744	!	no
35	3M-4 5	ı	l	1	l	ı	ı	3-120, 5-175	104	112	619	ŧ	ou
. 98	3M-5 m	ı	ı	ı	ı	ı	ı	3-120, 5-175	49	99	738	ı	ou
37	X8183/137 %	EM308 (70)	ı	1200	200	4.5	0.5	Room Temp	54*	155	891	.122 ± .038	no
38	ERL 0510 X	EM308 (70)	ı	800	400	4.5	0.3	Room Temp	53*	66	1081	.208 ± .049	no
39	EPON 828 &	EM308 (70)	ı	400	1	24	ı	Room Temp	50*	46	848	.256 ± .146	ou
40	X8183.137	MXDA (54)	ı	400	l	15	ì	Room Temp	63*	165	615	.280 ± .056	no
41	ERL 0510 H	MXDA (70)		80	l	20	i	Room Temp	47*	128	721	.414 ± .112	no
42	DEN 431	MXDA (39)	PHENOL (1.3	400	ı	7	ı	Room Temp	52*	82	704	.278 ± .120	yes
43	DER 332 LC	MXDA (40)	1	400	8	വ	~	Room Temp	404	52	918	.216 ± .070	Yes
44	R9-2039 FE	H2-3561	i	400	80	2.5	ı	Room Temp	37*	99	905	1.034 ± .096	Yes
	ı		* Tes	Tested aft	ter 4	Odav	O.	curing time at ro	room te	temperature	41146		

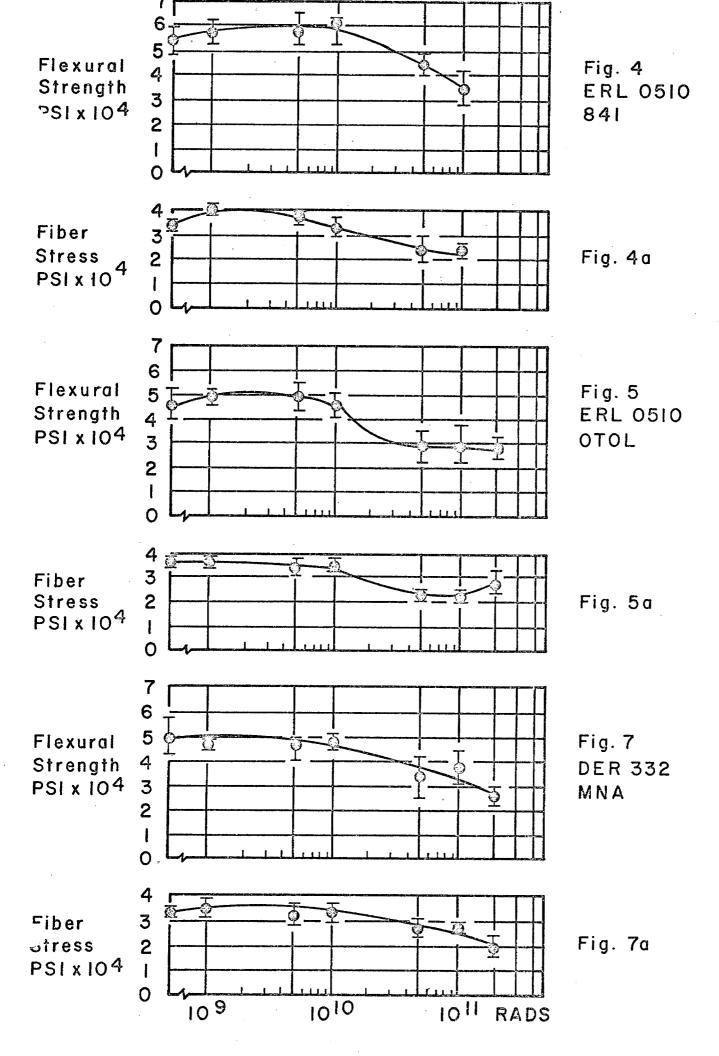
* Tested after 40 days curing time at room temperature

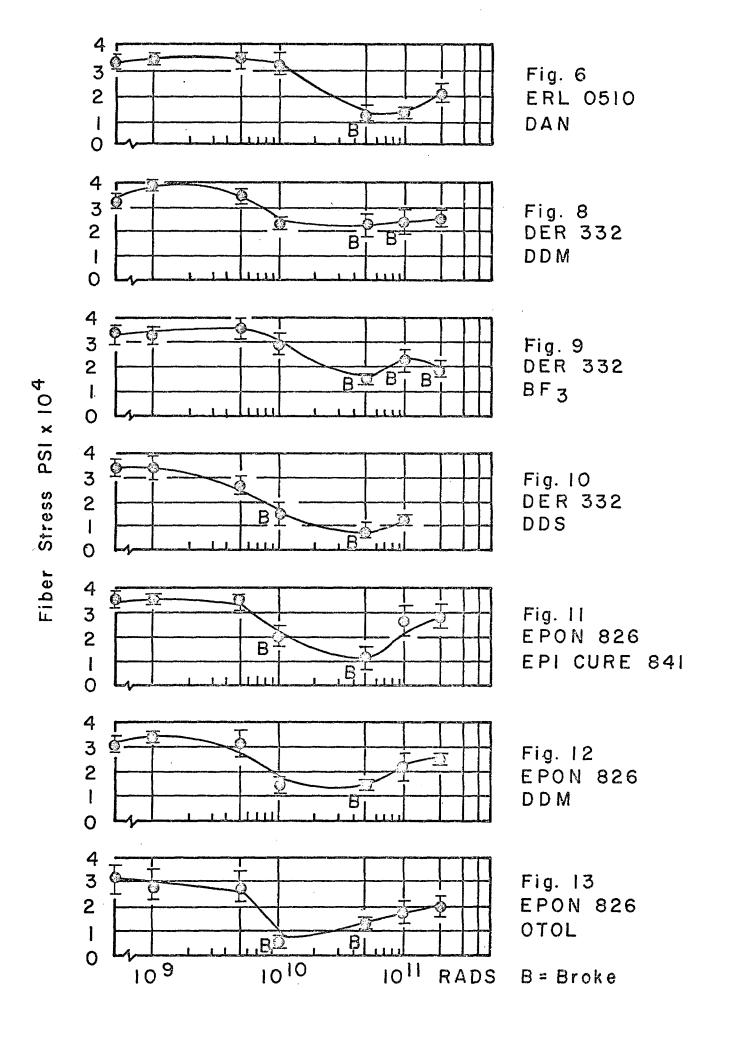
TABLE 5

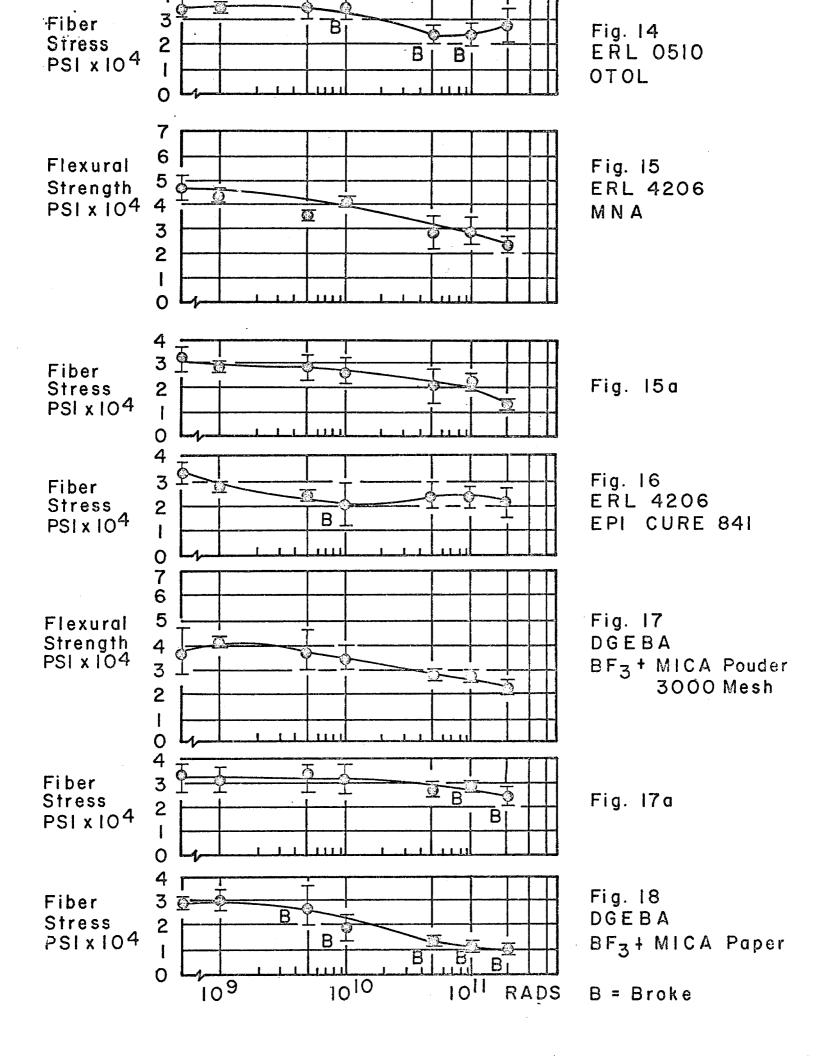
IZOD IMPACT STRENGTH OF EPOXY SYSTEMS WITH STOICHIOMETRIC,
DEFICIENT AND EXCESSIVE RATIO OF CURING AGENT

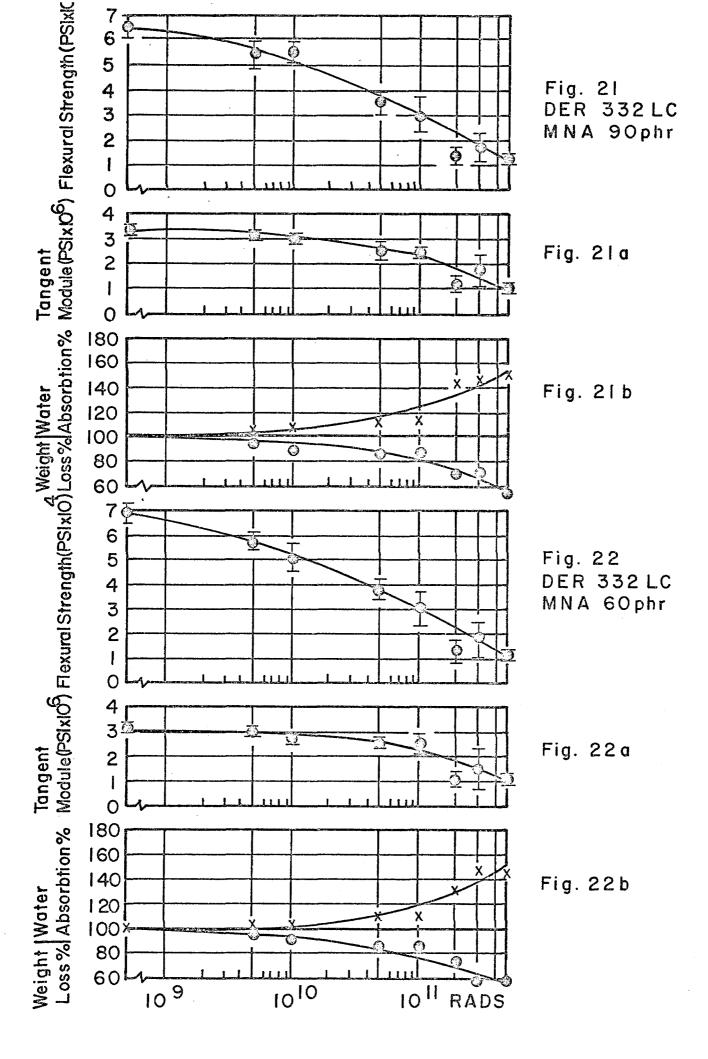
Sample Number	Resin	Curing Agent (phr.)	Accele- rator (phr.)	Curing Cycle hours - °C	Impact- Strength ft-lb/inch
21 22 31 23 31 32 31 31 31 31 31 31 31 31 31 31 31 31 31	DER 332 LC DER 332 LC DER 332 LC DER 332 LC EPON 826 EPON 826 EPON 826 DEN 431 DEN 431 DEN 431 DEN 431 DEN 431 DEN 438 TO T	MNA (90) MNA (60) MNA (135) MNA (90) MNA (56) MNA (135) 841 (25) 841 (17) 841 (38) MNA (85) MNA (85) MNA (57) MNA (128) MNA (55) MNA (128) 841 (24) 841 (16) 841 (36) MNA (120) MNA (80) MNA (180) 841 (35) 841 (53) MNA (205) MNA (205) MNA (157) 841 (86) MNA (120) MNA (80) MNA (180) 841 (57) 841 (86) MNA (120) MNA (80) MNA (180) 841 (57) 841 (86) MNA (120) MNA (80) MNA (180) 841 (51) MNA (90) MNA (90) MNA (90) MNA (225) 841 (43) 841 (29) 841 (60)	BDMA (1.9) BDMA (1.6) BDMA (2.5) BDMA (1.9) BDMA (1.6) BDMA (2.5)	4-80, 10-125 4-80, 10-125 4-80, 10-125 4-80, 10-125 4-80, 10-125 4-80, 10-125 6-150 22-160 6-150 22-160	.284 ± .031 .288 ± .047 .254 ± .042 .249 ± .070 .332 ± .048 .348 ± .040 .358 ± .056 .436 ± .132 .246 ± .050 .289 ± .058 .250 ± .033 .214 ± .010 .246 ± .028 .189 ± .104 .178 ± .036 .236 ± .037 .180 ± .037 .180 ± .037 .180 ± .038 .220 ± .042 .216 ± .010 .220 ± .040 .210 ± .028 .240 ± .028 .234 ± .027 .220 ± .028 .240 ± .028 .234 ± .027 .220 ± .028 .240 ± .028 .240 ± .028 .240 ± .028 .240 ± .028 .250 ± .058 too brittle to test .192 ± .020 .172 ± .018 .168 ± .030 .220 ± .048 .250 ± .030 .194 ± .038 .209 ± .012 .152 ± .050 .240 ± .029 .220 ± .036 .216 ± .053

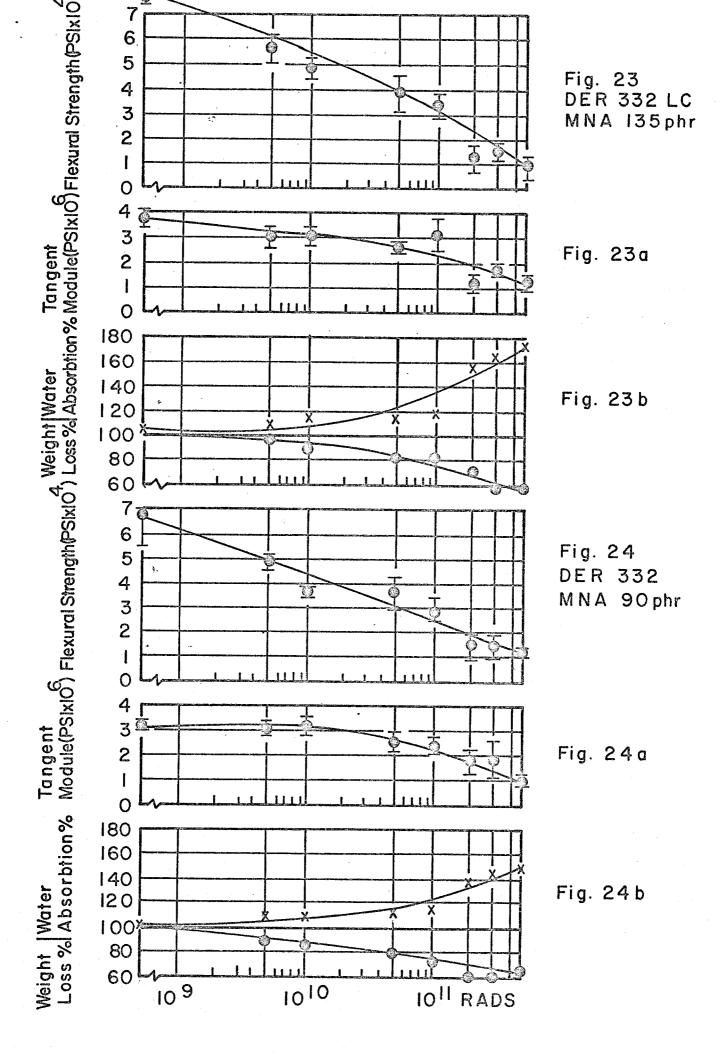


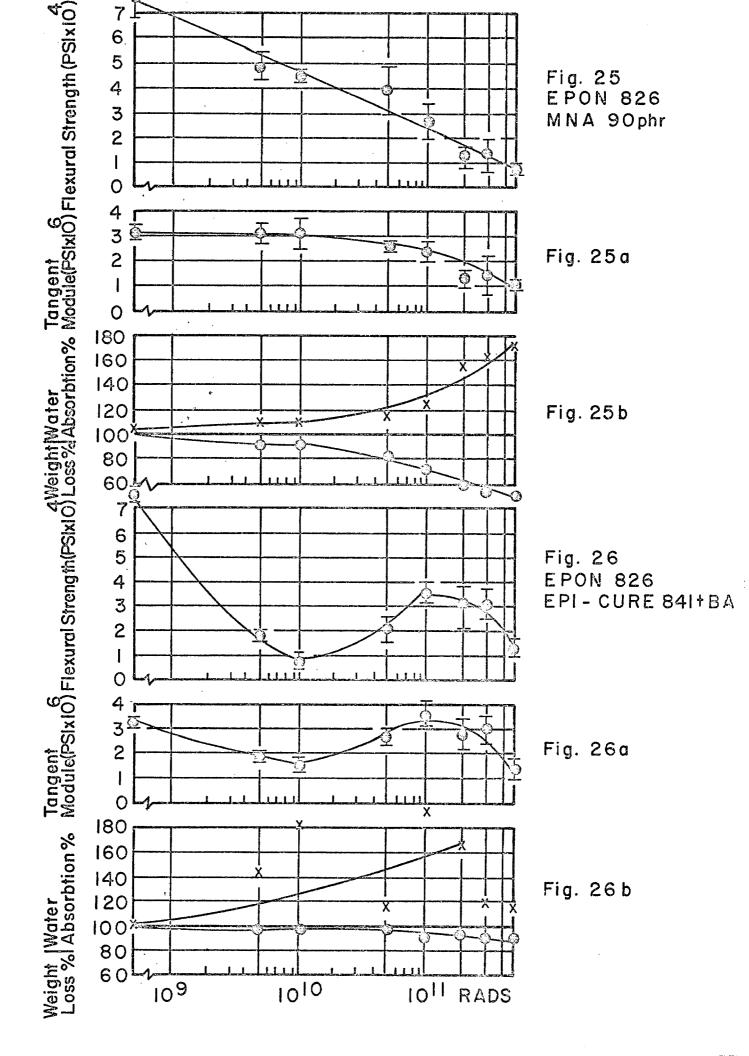


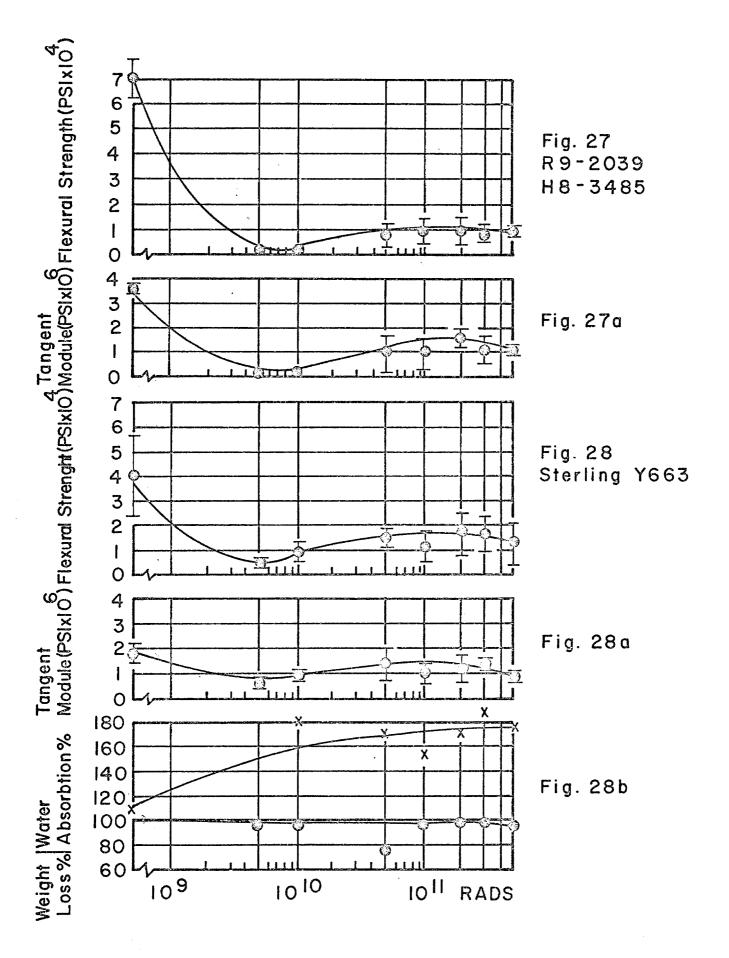


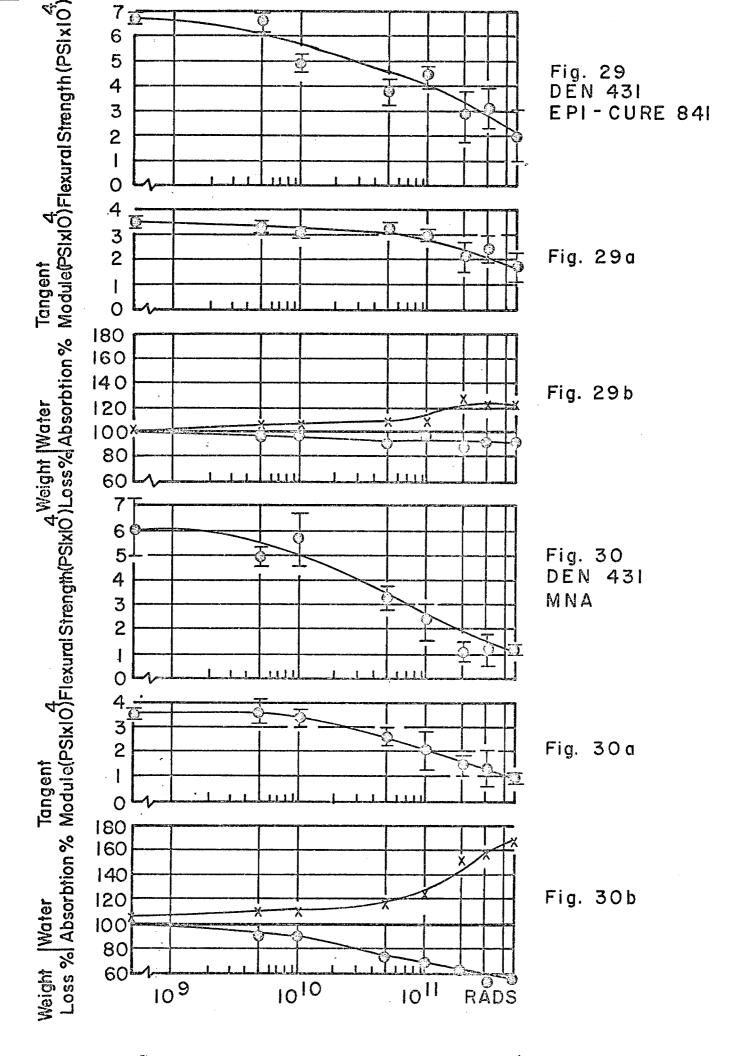


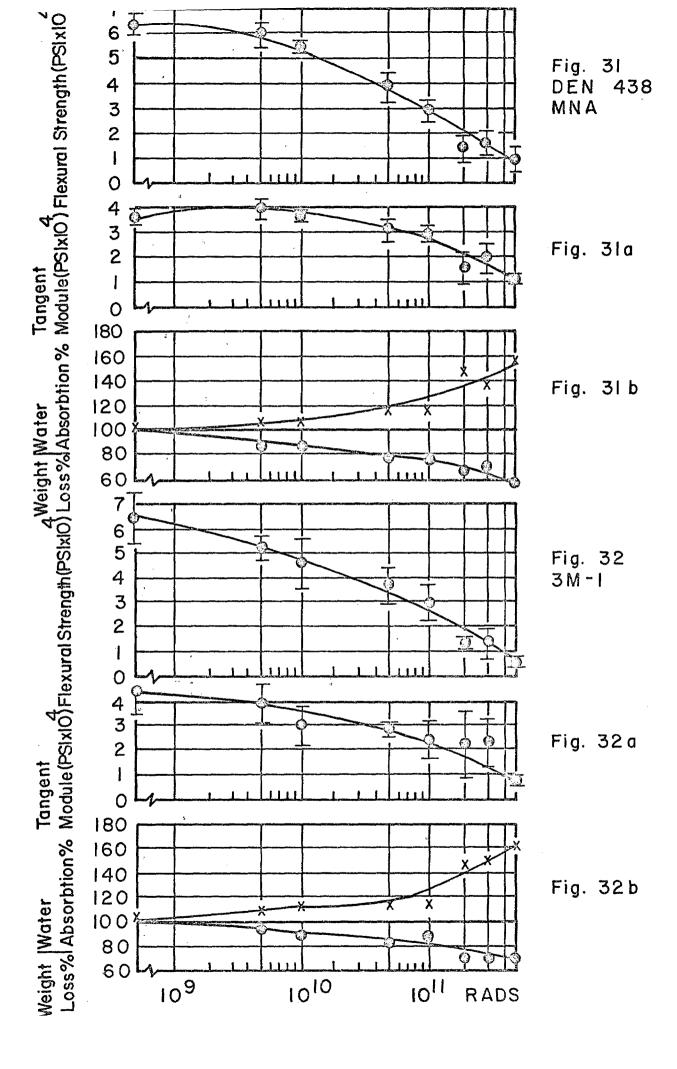


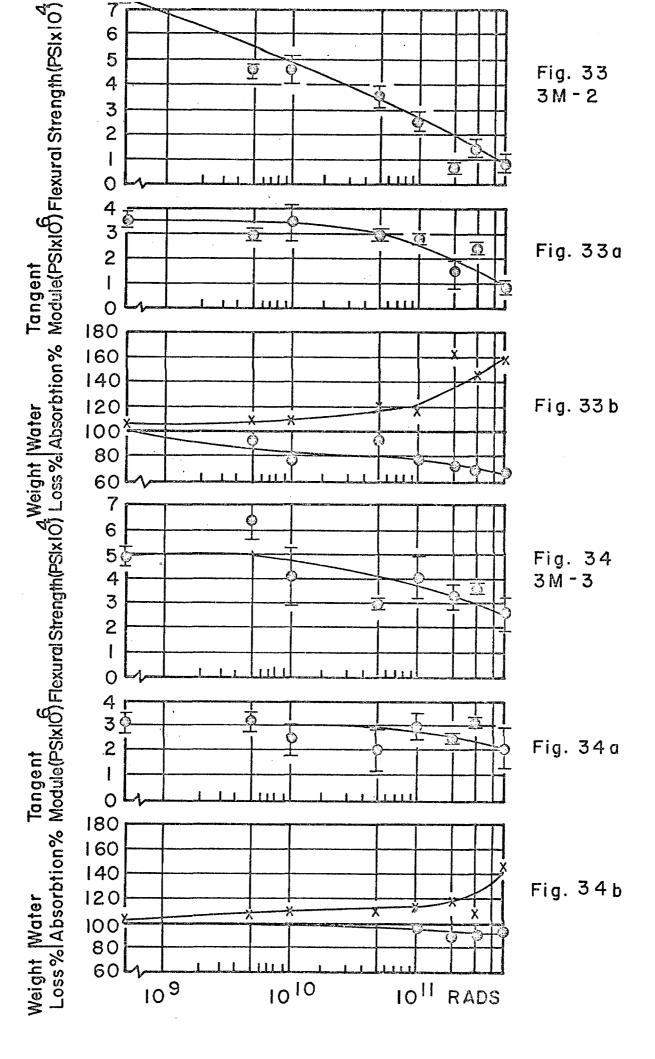


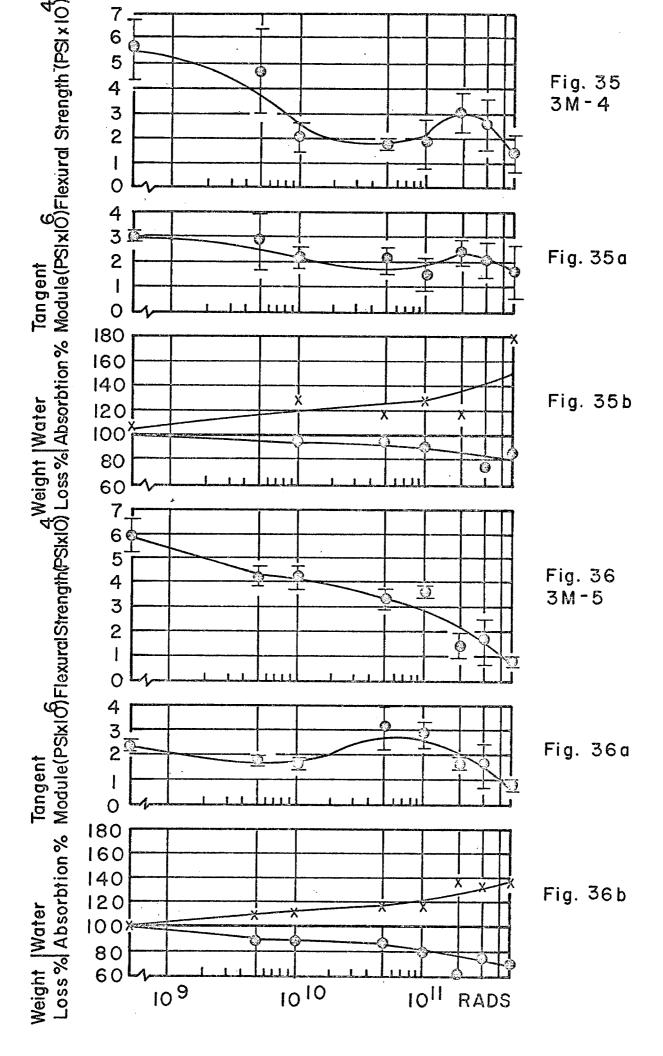


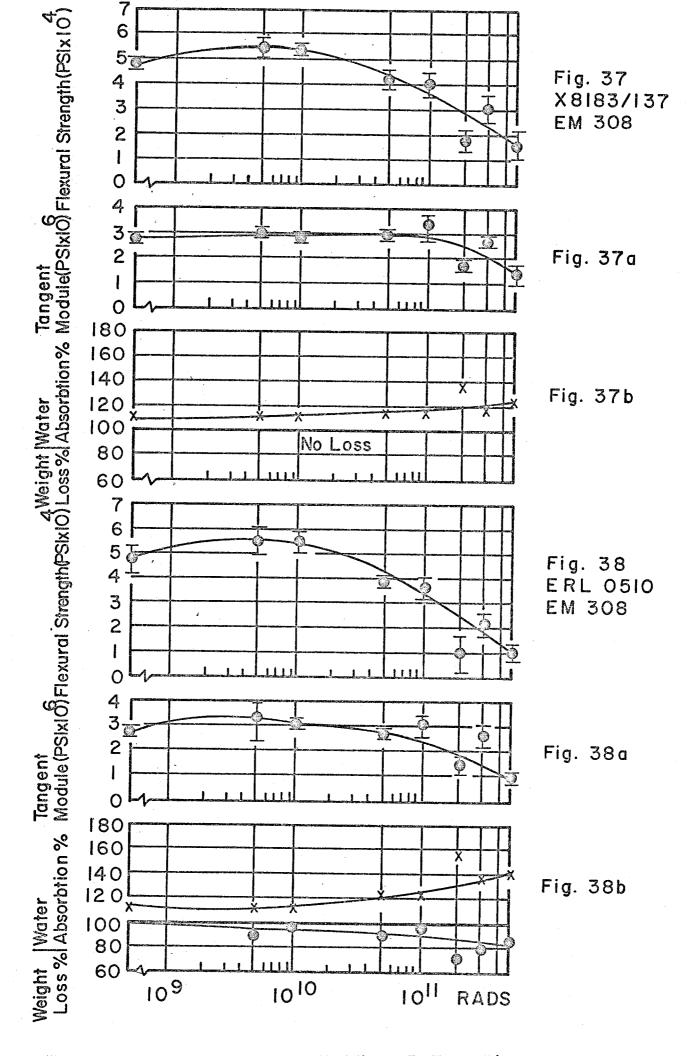


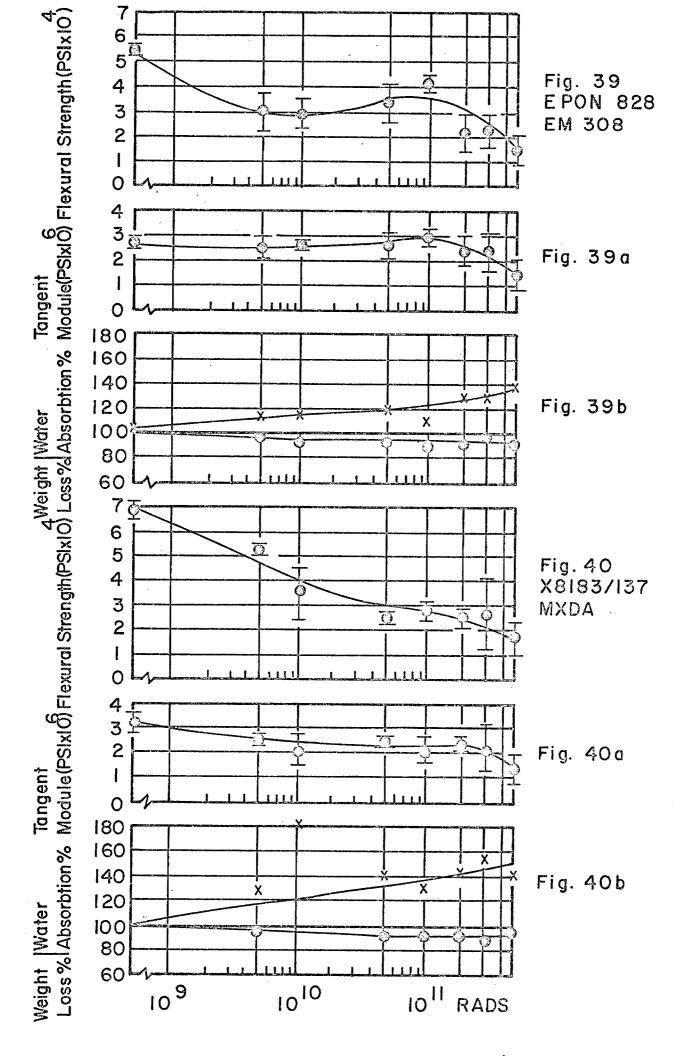


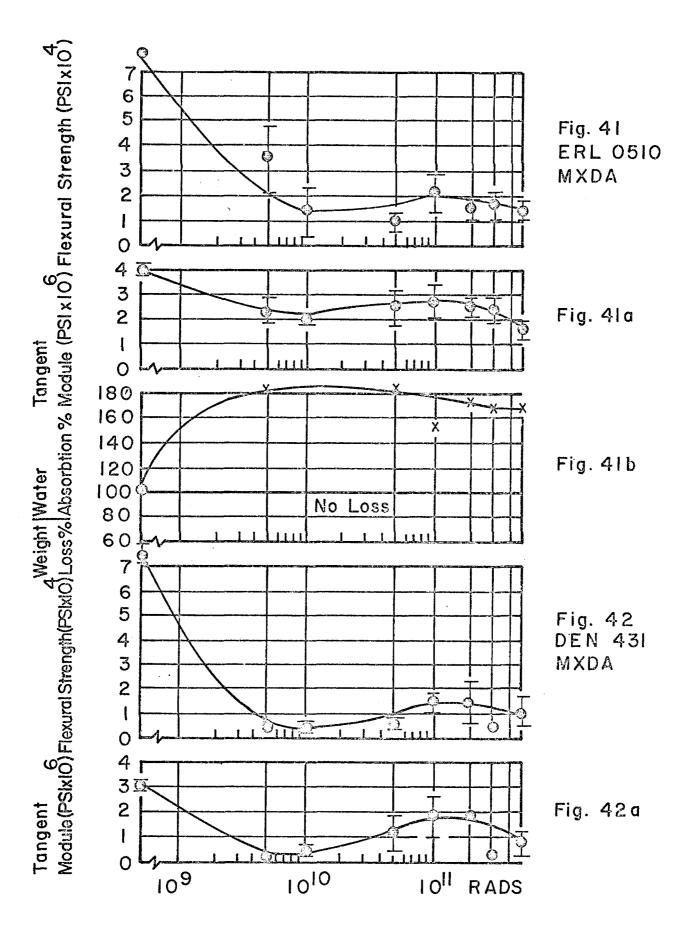


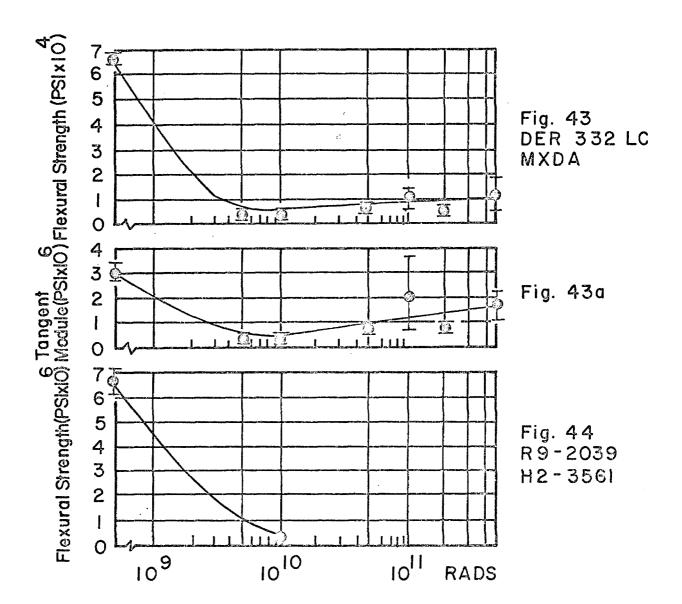












Ultimate Glass Transition Temperature, Flexural Strength, Water Absorbtion, 45 Figure

